

THE INFLUENCE OF DEUTERATION AND TURBULENT DIFFUSION ON THE OBSERVED D/H RATIO

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ABSTRACT

The influence of turbulent mixing on the chemistry of the interstellar medium (ISM) has so far received little attention. Previous studies of this effect have suggested that it might play an important role in mixing the various phases of the ISM. In this paper, we examine the potential effects of turbulent diffusion on the deuterium chemistry within molecular clouds. We find that such mixing acts to reduce the efficiency of deuteration in these clouds by increasing the ionization fraction and reducing freeze-out of heavy molecules. This leads to lower abundances for many deuterated species. We also examine the influence of turbulent mixing on the transition from atomic hydrogen to H₂ and from atomic deuterium to HD near the cloud edge. We find that including turbulent diffusion in our models serves to push these transitions deeper into the cloud and helps maintain a higher atomic fraction throughout the cloud envelope. Based on these findings, we propose a new process to account for the significant scatter in the observed atomic D/H ratio for galactic sightlines extending beyond the Local Bubble. Although several mechanisms have been put forward to explain this scatter, they are unable to fully account for the range in D/H values. We suggest a scenario in which turbulent mixing of atomic and molecular gas at the edges of molecular clouds causes the observed atomic D/H ratio to vary by a factor of ~ 2 .

Key words: astrochemistry – diffusion – ISM: abundances – ISM: clouds – ISM: molecules – turbulence

Online-only material: color figures

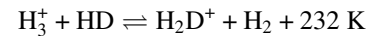
1. INTRODUCTION

Since the first detection of a deuterium-bearing molecule, DCN, by Jefferts et al. (1973), it has become clear that the fraction of deuterium contained in molecules can be extremely high in the dense interstellar medium (ISM), with abundances of some deuterated species observed to be comparable to those of their hydrogenated counterparts. This is in stark contrast to the low atomic D/H ratio measured by absorption studies in the diffuse gas, which has an average value of $(1.56 \pm 0.04) \times 10^{-5}$ (i.e., 15.6 ± 0.4 ppm) in the local ISM (Wood et al. 2004).

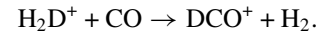
The discovery of multiply deuterated molecules provided remarkable evidence to support the high molecular D/H ratios observed. Based on the elemental D/H ratio, such species would be expected to have abundances of order 10^{-10} or less, relative to their hydrogenated analogs. Yet doubly deuterated ammonia, ND₂H, was found to have an abundance ratio [ND₂H]/[NH₃] of 0.5% in the dark cloud L134N (Roueff et al. 2000) and 3% in the prestellar core 16293E (Loinard et al. 2001). Similarly, [D₂CO]/[H₂CO] ratios ranging from 1% to 40% have been observed in low-mass protostars and prestellar cores (Ceccarelli et al. 1998; Loinard et al. 2002; Bacmann et al. 2003). Subsequent detections of CHD₂OH (Parise et al. 2002), D₂S (Vastel et al. 2003), and D₂H⁺ (Vastel et al. 2004) showed similarly high abundance ratios. Amazingly, molecules bearing three deuterons have also been detected, the first of which, triply deuterated ammonia, was observed to have an abundance ratio [ND₃]/[NH₃] $\sim 0.1\%$ in the dark cloud Barnard 1 (Lis et al. 2002) and in the Class 0 protostar NGC 1333 IRAS 4A (van der Tak et al. 2002). Triply deuterated methanol, CD₃OH, has also been detected in the low-mass protostar IRAS 16293–2422 with an abundance ratio [CD₃OH]/[CH₃OH] $\sim 1\%$ (Parise et al. 2004). Such extreme enhancement of the D/H ratio within molecules points to the dramatic efficiency of deuterium frac-

tionation in cold dense molecular clouds, a process that was first proposed by Solomon & Woolf (1973).

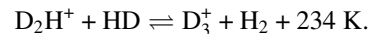
At the low temperatures found in the cores of molecular clouds (~ 10 K), the process of fractionation acts to minimize the zero-point vibrational energy of molecules by swapping constituent atoms for their heavier isotopes. Exchange reactions therefore lead to the preferential substitution of H by D in molecules. Most gas-phase chemistry proceeds via ion–molecule reactions, the most important ion of which is H₃⁺. Deuteration of this species through the reaction



is also preferred at low temperatures (Watson 1976). Reactions with abundant gas-phase species, such as CO, O, and N₂, transfer the deuteron to other molecules and limit the amount of H₂D⁺ that can be maintained, e.g.,



In order for deuteration to proceed further and allow the formation of multiply deuterated species, H₂D⁺ must survive long enough for it to undergo subsequent deuteron exchange:



This is possible when the atoms and molecules that destroy it are removed from the gas phase by freeze-out onto grain surfaces (Brown & Millar 1989; Roueff et al. 2000; Roberts & Millar 2000b). This occurs in the cold dense regions of the ISM and the resulting depletion of abundant species, such as CO, has been observed in many sources (e.g., Willacy et al. 1998; Kramer et al. 1999; Caselli et al. 1999; Bergin et al. 2002; Bacmann et al. 2002; Tafalla et al. 2004). Direct evidence for

the link between freeze-out and enhanced deuteration comes from the observed correlation between CO depletion and the $[D_2CO]/[H_2CO]$ ratio (Bacmann et al. 2003).

Grain-surface deuteration occurs by hydrogen abstraction and deuterium addition to mantle species on dust grains (Tielens 1983). This requires a reservoir of atomic deuterium to be maintained in the gas. This, again, is produced as a result of the $H_3^+ \rightarrow H_2D^+ \rightarrow D_2H^+ \rightarrow D_3^+$ series of reactions, with atomic deuterium a product of the dissociative recombination of these ions. For a more detailed discussion of deuterium chemistry, see, e.g., Roberts et al. (2003, 2004), Phillips & Vastel (2003), and Phillips & Lis (2006).

Studies of the atomic D/H ratio in the local ISM provide an important constraint for models of galactic chemical evolution and insight into the processing of primordial gas up to the present era. Values for the galactic D/H ratio are obtained by deriving column densities of D I and H I from observed Lyman series absorption lines in interstellar gas toward background stars. Since the first of these measurements were carried out, an unexpectedly large variation has emerged for sightlines extending beyond the Local Bubble, with values ranging from 5 to 22 ppm (see, e.g., Linsky et al. 2006, for a recent discussion). This significant scatter is at odds with the more uniform values obtained for the primordial D/H ratio, as probed by quasar absorption line systems and inferred from cosmic microwave background anisotropy data. These methods have yielded a fairly consistent value of $(D/H)_{\text{prim}} = 27.5^{+2.4}_{-1.9}$ ppm (see, e.g., Cyburt et al. 2003).

Other than big bang nucleosynthesis, no formation mechanism for deuterium is known to exist, and explanations for the varying D/H ratio therefore focus on ways to destroy or hide the deuterium. A corollary of this is that the highest observed values for the D/H ratio must be closest to the true value. The process of astration—the conversion of deuterium to ^3He , ^4He , and heavier elements via stellar nucleosynthesis—has long been proposed to explain the generally low values for the atomic D/H ratio measured in the Galaxy, with differences in the degree of processing of the ISM being suggested as an explanation for the observed scatter. An alternative theory has been proposed by Draine (2004, 2006) in which deuterium atoms deplete onto dust grains in quiescent regions of the ISM and are subsequently returned to the gas phase if the grain mantles are destroyed. The observed correlation between metal depletion and decrease in the D/H ratio has been used to support this theory (Prochaska et al. 2005; Linsky et al. 2006; Steigman et al. 2007), which predicts that regions that have experienced some degree of dust destruction should display both higher gas-phase abundances of refractory metals (titanium, iron, silicon, etc.) and higher D/H ratios (owing to the removal of both metals and deuterium from the grains). There are, however, outliers in these trends that disrupt the correlation and cannot be explained by simple dust depletion models. One important process acts to increase the D/H ratio, namely, the galactic infall of nearly pristine (i.e., unprocessed) material (see, e.g., Prodanović & Fields 2008; Tosi 1996). If the infalling material is not fully mixed with the existing ISM, these inhomogeneities can also lead to variations in the observed D/H ratio.

It is well established that molecular clouds are turbulent and that turbulence plays an important—perhaps even dominant—role in governing the dynamics and support of these clouds. What is less certain is the extent to which turbulent eddies can transport the gas and dust within a cloud, disrupting the abundance profiles predicted by static chemical models and

redistributing the atomic and molecular species. The effects of turbulence on cloud chemistry were first considered by Phillips & Huggins (1981). Subsequent work on this subject (e.g., Boland & de Jong 1982; Federman & Allen 1991; Xie et al. 1995; Willacy et al. 2002; Lesaffre et al. 2007) has demonstrated that turbulent mixing under conditions that are typical of molecular clouds can lead to “smearing out” of the abundance gradients, reducing the variation with depth as the gas is transported between the cloud envelope and its interior.

Turbulent transport in molecular clouds is a diffusive process (often called eddy diffusion; see, e.g., Hinze 1975) and the model employed in this work is derived from atmospheric chemical models in which the rate of turbulent transport for a given molecule depends on its abundance gradient. Such models describe the turbulent mixing between adjacent zones as a Fickian diffusion process with a diffusion coefficient K derived from mixing length theory (Taylor 1915; Prandtl 1925), a phenomenological approach analogous to the concept of the mean free path in thermodynamics. For full details of this model, the reader is referred to the description contained in the original paper by Xie et al. (1995).

As already discussed, the process of deuterium fractionation is extremely efficient at altering the D/H ratio of molecules in the cold, dense cores of molecular clouds. Indeed, Phillips & Lis (2006) suggest that this process may lead to a significant fraction of deuterium being locked in molecules in cloud centers. Meanwhile, at the edges of these clouds and in diffuse regions of the ISM, where the gas is warm and purely atomic, the observed atomic D/H ratio should reflect the “true” elemental value (neglecting, for the moment, the possibility that deuterium may be also depleted onto dust grains). Turbulent diffusion serves to mix these two phases of the ISM—the warm diffuse material at the edge of clouds and the cold dense material in their centers—and in so doing, may alter the atomic D/H ratio observed at the cloud edge, as well as that in the cloud center. If this is the case, then the observed atomic D/H ratio along a particular line of sight will depend on a number of factors: (1) the degree of astration that the material along that sightline has been subjected to; (2) the amount of deuterium that has been depleted onto dust grains; (3) the efficiency of chemical fractionation in the gas along the sightline; (4) the degree of turbulent mixing of the different phases of the ISM; and (5) the proximity of the line of sight to a molecular cloud. In general, these mechanisms act to lower the value of the observed atomic D/H ratio. Therefore, the highest observed value must be closest to the true elemental abundance ratio.

We have examined the effects of turbulent diffusion on deuterium chemistry within molecular clouds and the resulting change in the abundances of key deuterated species. We also propose a process by which the variation in the measured atomic D/H ratio along diffuse lines of sight can be explained by turbulent mixing of the gas observed along these sightlines with denser material in neighboring regions. We describe the modifications made to the existing model for this work and the physical parameters of the cloud models considered in Section 2. The results of these models are presented in Section 3 and their implications for the observed D/H ratio are discussed in Section 4. Finally, we summarize our findings in Section 5.

2. THE MODEL

The models used in this work are extensions of those described in Xie et al. (1995) and Willacy et al. (2002). The

Table 1
Initial Abundances

Species	n_i/n	Species	n_i/n
H	1.00	He	0.14
D	1.60×10^{-5}	C ⁺	7.30×10^{-5}
N	2.14×10^{-5}	O	1.76×10^{-4}
Mg ⁺	7.00×10^{-9}	Fe ⁺	3.00×10^{-9}

Note. $n = n(\text{H}) + 2n(\text{H}_2)$.

Table 2
Cloud Parameters

Model	r_0 (pc)	n_0 (cm ⁻³)	T_{out} (K)	T_{in} (K)
1	1.11	888	10	10
2	4.00	250	100	10

reader is referred to those papers for a detailed description of the implementation of turbulent diffusion in the model.

The diffusive transport appears as an additional term in the continuity equation for each species, at each depth step,

$$\frac{\partial n_i}{\partial t} = P_i - L_i - \frac{\partial \phi_i}{\partial r}, \quad (1)$$

where n_i is the number density of species i , P_i and L_i are its production and loss terms, respectively, and ϕ_i is its net transport flux in the radial direction, given by

$$\phi_i \text{ (cm}^{-2} \text{ s}^{-1}\text{)} = -Kn \frac{\partial x_i}{\partial r}, \quad (2)$$

where n is the total proton number density [$n = n(\text{H}) + 2n(\text{H}_2)$], $x_i = n_i/n$ is the fractional abundance of species i , and K is the turbulent diffusion coefficient (cm² s⁻¹). All quantities are depth and time dependent, with the exception of the diffusion coefficient, which we assume to be constant across the cloud.

The strength of turbulent mixing in the model is governed by the turbulent diffusion coefficient K . It is difficult to accurately determine values for K , since the nature of turbulence in molecular clouds is still unclear. However, it is possible to derive an order-of-magnitude estimate for K by assuming $K \sim \langle V_L L \rangle$, where V_L is the turbulent velocity and L is the correlation length of the diffusive process (see Xie et al. 1995, for details). Based on estimates of the correlation length in molecular clouds (0.1–0.5 pc) and typical turbulent velocities (0.1–1 km s⁻¹), we consider values of K between 0 (i.e., no diffusion) and 10^{23} cm² s⁻¹.

In this work, our aim is to explore the potential impact of turbulent mixing on deuterium fractionation, rather than to make quantitative predictions for the resulting changes in abundances or fractionation ratios. Precise values of K are therefore not important and we focus instead on exploring the plausible range of values that might be expected.

The chemical network used in the model includes gas-phase and grain-surface reactions, freeze-out onto grain surfaces, and evaporation of mantle species. We adopt the gas-phase reaction rates of the RATE99 release of the UMIST database for astrochemistry (Le Teuff et al. 2000). The treatment of freeze-out, grain-surface chemistry, and desorption mechanisms are described in Willacy (2007). We include the effects of thermal evaporation and cosmic-ray-induced desorption, and consider grain-surface reactions involving the addition of atoms and CH,

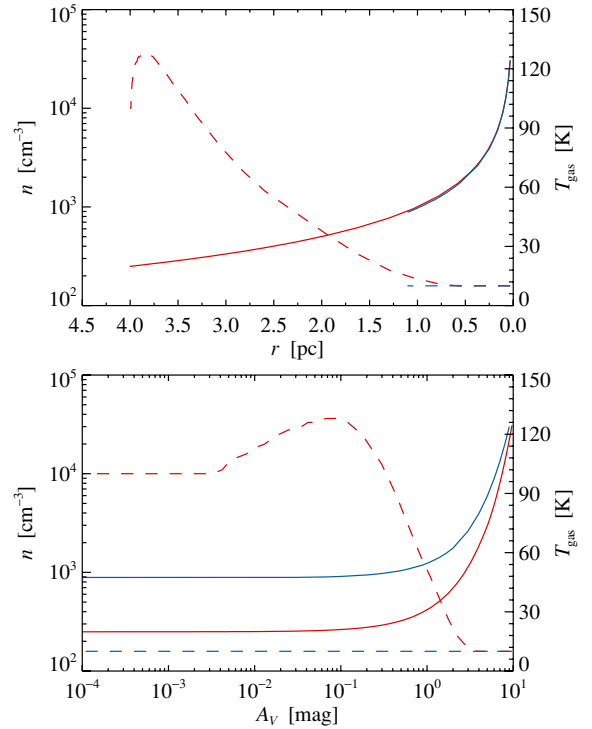


Figure 1. Cloud densities (solid lines) and gas temperatures (dashed lines) adopted in model 1 (blue) and model 2 (red). The top plot shows the radial dependence of these cloud properties and the bottom plot shows their variation as a function of visual extinction into the cloud.

(A color version of this figure is available in the online journal.)

OH, and NH radicals to grain mantle species, as well as their deuterated analogs. The migration of H and D across grain surfaces is assumed to be governed by the relatively slow hopping between surface sites. Using slow rates with a rate equation model has been shown by Vasyunin et al. (2009) to give good agreement with more exact Monte Carlo models of grain-surface chemistry. The model also considers the effects of an external interstellar radiation field (ISRF) on the chemistry, including photodissociation and photoionization of gas-phase species and photoevaporation of mantle species from grain surfaces. Self-shielding by H₂ increases the attenuation of dissociating far-ultraviolet (FUV) radiation, causing its photodissociation rate to drop rapidly with increasing depth into the cloud. We adopt the standard ISRF determined by Draine (1978) and the H₂ self-shielding treatment of Lee et al. (1996). HD does not self-shield, but some of its lines do overlap with those of H₂. This means that H₂ can provide some shielding. Here we follow the approach of Barsuhn (1977) who estimated that the overlap of HD and H₂ lines would reduce the HD photodissociation rate by 1/3, assuming that the overlapped HD lines are totally shielded by the H₂ lines.

The initial gas-phase elemental abundances used in all models are listed in Table 1. Initial abundances for all other species are assumed to be zero. We adopt the average elemental deuterium abundance determined for the Local Bubble (1.6×10^{-5} ; Wood et al. 2004). Although this value is only valid locally, the true elemental deuterium abundance for the galactic disk is unknown (and likely to be higher). The effect of an increased deuterium abundance on the deuterium fractionation has been investigated by Roueff et al. (2007) who find that it leads to a corresponding linear increase in the deuteration of molecules.

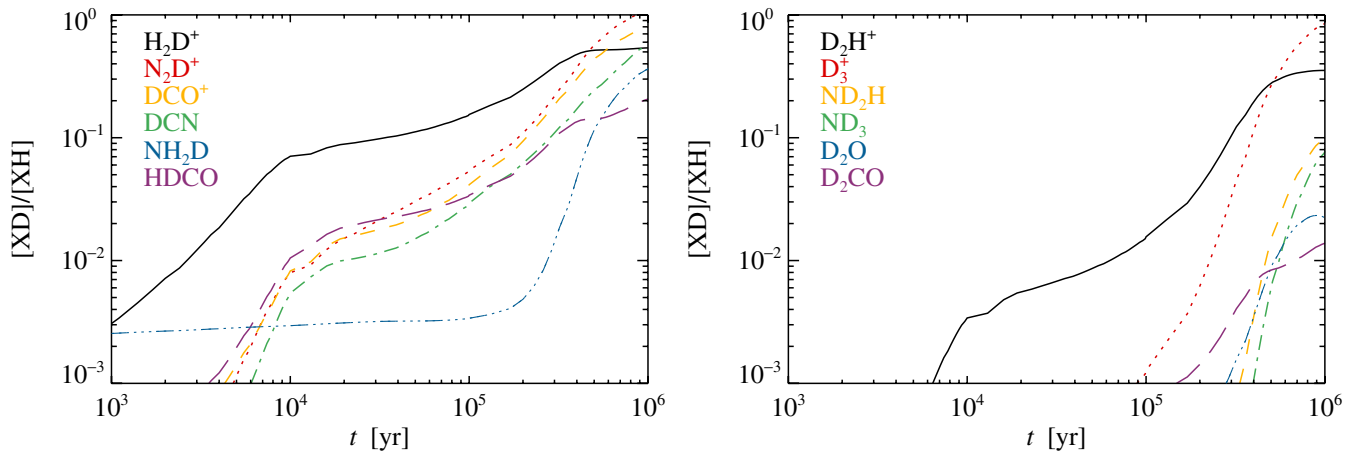


Figure 2. Fractionation ratios for various deuterated species at the cloud center, as a function of time. The left-hand plot shows results for a number of singly deuterated species, H_2D^+ (black, solid), N_2D^+ (red, dotted), DCO^+ (yellow, dashed), DCN (green, dot-dashed), NH_2D (blue, triple dot-dashed), and HDCO (purple, long-dashed). The right-hand plot shows results for various doubly and triply deuterated species, D_2H^+ (black, solid), D_3^+ (red, dotted), ND_2H (yellow, dashed), ND_3 (green, dot-dashed), D_2O (blue, triple dot-dashed), and D_2CO (purple, long-dashed). Results for model 1 are shown.

(A color version of this figure is available in the online journal.)

2.1. Changes to the Model

The major modifications to the code necessary for this work were the introduction of deuterated species into the network of chemical reactions and the inclusion of freeze-out, grain surface chemistry, and desorption processes. The treatment of deuterium chemistry and these additional processes is described in detail in Willacy (2007).

2.2. Cloud Properties

In order to investigate the effects of turbulent diffusion under different interstellar environments, we have applied our code to two distinct sets of cloud parameters, which we list in Table 2. We assume a density profile of the form $n(r) = n_0(r_0/r)$ in both models. Since the code does not attempt to solve the thermal balance within the cloud, we impose fixed temperature profiles on the gas and dust. The models are distinct in the following ways. In model 1, which is identical to that used previously by Xie et al. (1995) and Willacy et al. (2002), we adopt a cloud size of $r_0 = 1.11$ pc (3.41×10^{18} cm), a number density at the cloud edge of $n_0 = 888 \text{ cm}^{-3}$, and a constant gas and dust temperature of 10 K (i.e., $T_{\text{in}} = T_{\text{out}} = 10$ K). Model 2 attempts to simulate a more extended cloud, with a larger, diffuse envelope extending to $r_0 = 4.0$ pc (1.23×10^{19} cm) and a density at its edge of $n_0 = 250 \text{ cm}^{-3}$. To account for the higher temperatures present in diffuse cloud envelopes, the temperature profile used in model 2 was determined using a separate code, designed to calculate the chemical and thermal structure of photon-dominated regions (PDRs) by treating the depth-dependent chemistry, heating, and cooling simultaneously (see Bell et al. 2006 for details). The same chemical network and incident radiation field were used in the PDR code and the density profile for model 2 was adopted. The resultant temperature profile initially rises sharply from $T_{\text{out}} = 100$ K at the cloud edge to ~ 130 K at a radius of 3.8 pc, before gradually falling to $T_{\text{in}} = 10$ K at the cloud center. The gas density and temperature profiles for models 1 and 2 are shown in Figure 1. In both models, the dust temperature is assumed to be constant at 10 K throughout the cloud. We note that, while this may only be truly valid for the dense central regions, the choice of dust temperature in the cloud envelope has less of an impact on the chemistry

because freeze-out is less effective at the lower densities found there.

In all models, the chemical evolution of the cloud is computed for a period of 1 Myr. The results are discussed in the following section, where all abundances are quoted relative to the total proton number density, $n = n(\text{H}) + 2n(\text{H}_2)$.

3. RESULTS

Before examining the effects of turbulent diffusion on the deuterium chemistry, it is important to compare the results of our static chemical model to previous theoretical work and to observations. Chemical models with increasingly sophisticated treatment of the deuterium fractionation and freeze-out have been constructed over the years (e.g., Roberts & Millar 2000a, 2000b; Rodgers & Charnley 2001; Roberts et al. 2003; Flower et al. 2004, 2006a, 2006b; Aikawa et al. 2005; Roueff et al. 2007). These are generally time dependent, but often limited to a single spatial point with conditions appropriate for the centers of dark clouds, characterized by low temperature ($T \sim 10$ K), high density ($n \geq 10^4 \text{ cm}^{-3}$), and high visual extinction ($A_V \sim 10$ mag). Most of these models do not consider the more extended envelopes of molecular clouds, where temperatures are higher and densities lower, and the material is exposed to the ISRF (however, see Le Petit et al. 2002). For the purposes of comparison, we show in Figure 2 the fractionation ratios of a number of deuterated species at the center of our model cloud, as a function of time. In this paper, we use the term “fractionation ratio,” or $[\text{XD}]/[\text{XH}]$, to mean the abundance ratio of a deuterated species with respect to its fully hydrogenated counterpart. It can be seen that fractionation ratios for many deuterated species approach values of $\sim 10\%$ or higher at the cloud center after 1 Myr of chemical evolution. Particularly impressive are N_2D^+ , which reaches a higher abundance than N_2H^+ , and ND_3 , whose abundance is comparable to ND_2H . In contrast, the fractionation ratios at the outer edge of the cloud are $\sim 0.1\%$ or less for most deuterated species.

The majority of models described in the literature employ much higher number densities than are considered here (typically of order 10^6 cm^{-3} , whereas our central cloud density is $3 \times 10^4 \text{ cm}^{-3}$). This makes a direct comparison difficult.

Table 3

Model Fractionation Ratios for Selected Species and Typical Observed Values

Species	Model ^a $N(\text{XD})/N(\text{XH})$ (%)	Observed $[\text{XD}]/[\text{XH}]$ (%)	References
H ₂ D ⁺	28
D ₂ H ⁺	12
D ₂ H ⁺ /H ₂ D ⁺	42	50–100	1 ^b
N ₂ D ⁺	19	10–30	2, 3
DCO ⁺	15	4–18	4, 5
DCN	9	4–6	2, 6
DNC	4	2–9	2, 7
NH ₂ D	10	10–30	5, 8, 9
ND ₂ H	2	0.5–4	9, 10, 11
ND ₃	0.9	0.02–0.55	9, 12, 13
HDO	8	0.2–3	14
D ₂ O	0.2
HDCO	6	3–7	2, 6
D ₂ CO	0.2	1–10	15, 16

Notes.

^a Model fractionation ratios are determined from total column densities integrated over all radial points in model 1 at 1 Myr.

^b Observed fractionation ratios for H₂D⁺ and D₂H⁺ do not exist in the literature, but the $[\text{D}_2\text{H}^+]/[\text{H}_2\text{D}^+]$ ratio has been measured in the prestellar core 16293E by Vastel et al. (2004).

References. (1) Vastel et al. 2004; (2) Turner 2001; (3) Gerin et al. 2001; (4) Williams et al. 1998; (5) Tiné et al. 2000; (6) Roberts et al. 2002; (7) Hirota et al. 2003; (8) Hatchell 2003; (9) Roueff et al. 2005; (10) Roueff et al. 2000; (11) Loinard et al. 2001; (12) Lis et al. 2002; (13) van der Tak et al. 2002; (14) Parise et al. 2005; (15) Bacmann et al. 2003; (16) Roberts & Millar 2007.

Roberts et al. (2003) performed detailed chemical modeling that included multiply deuterated species and freeze-out of gas-phase species onto grain mantles. They considered models with $T = 10$ K and $n(\text{H}_2) = 10^4 \text{ cm}^{-3}$, conditions very similar to those in the center of our model cloud. In order to compare our chemical model to theirs, we ran a single depth-step model with the same physical conditions and initial abundances as used in their paper. Comparing the fractionation ratios listed in their Table 1 with the values from our single-point model at $t = 1$ Myr, the two models agree within a factor of two for most deuterated species, the only exception being ND₃, which is an order of magnitude higher in our model. This disagreement is probably due to differences in the choice of branching ratios in the chemical networks. A detailed analysis of the differences between our model and those of others is beyond the scope of this paper, but despite these minor differences, we consider our model to be in good agreement with the results of Roberts et al. (2003).

When comparing our results to observational data, it is more appropriate to consider fractionation ratios based on total column densities through the model cloud, since observed fractionation ratios are determined in the same way. We therefore list in Table 3 the fractionation ratios for various species in the model determined from total column densities, $N(\text{XD})/N(\text{XH})$, alongside the typical range of observed values quoted in the literature. The general agreement is very good, with model fractionation ratios for most species falling within, or very close to, the observed range of values. The notable exceptions are HDO, the bulk of which is expected to be in the form of ice, and D₂CO, which is typically observed in warmer sources or regions of higher density (Bacmann et al. 2003). The model values generally fall at the lower end of the observed ranges, which is to be

expected, since the majority of the observed sources have much higher central densities.

Our intention in this paper is to examine the general effects of introducing turbulent diffusion into models of deuterium chemistry in the ISM, focusing on overall trends, rather than making quantitative predictions for specific sources. With this in mind, we regard the results of our deuterium model to be in good agreement with previous models and observations.

3.1. General Trends

We find that turbulent mixing can often lead to unintuitive effects on the deuterium chemistry, reducing the level of deuteration in some species, while enhancing that of others at certain points within the cloud. This is due to the complex interplay between mixing and chemical processes, redistributing important feed molecules that govern the deuterium chemistry, while disrupting the freeze-out of abundant species such as CO that can hinder deuteration of gas-phase species.

To illustrate the predicted effects of turbulent diffusion on the deuterium chemistry, we show in Figure 3 the fractionation ratios of a number of important deuterated molecules (at $t = 1$ Myr) as a function of visual extinction into the cloud for a set of models with diffusion coefficients of $K = 0$ (i.e., no diffusion) to $K = 10^{23} \text{ cm}^2 \text{ s}^{-1}$ (an upper limit to the possible range of values). It is immediately obvious that increasing levels of turbulent diffusion generally act to reduce the abundances of deuterated molecules. In the cloud center ($A_V > 1$ mag), all deuterated species suffer under the influence of turbulent diffusion, with fractionation ratios dropping by up to several orders of magnitude. However, the effect is not uniform throughout the cloud, and in the envelope, the deuteration of some species actually increases when turbulent mixing is active. In the following two sections, we consider the effects of turbulent diffusion on the cloud center and envelope separately.

3.2. Cloud Core

Turbulent diffusion limits the abundance of deuterated species in the cloud center by disrupting two of the key features that are important for effective deuteration.

1. The ionization fraction (electron abundance) is enhanced.
2. Depletion of gas-phase species onto grains is reduced.

Together, these lead to significantly lower abundances of H₂D⁺, D₂H⁺, and D₃⁺ compared to chemical models that do not include turbulent mixing, in turn resulting in lower abundances of the deuterated molecules that are formed from these ions.

Figure 4 shows the fractional abundance of electrons as a function of visual extinction in both models, for values of K from 0 (no diffusion) to $10^{23} \text{ cm}^2 \text{ s}^{-1}$ (strong diffusion). The electron abundance in the cloud center rises by a factor of four when $K = 10^{23}$, compared to models in which diffusion is absent. This is due to the influx of ions and electrons from the cloud surface, where species such as carbon are rapidly photoionized by the unattenuated flux of FUV photons.

Turbulent diffusion also acts to reduce the level of freeze-out in the cold dense cloud core. This is caused by movement of the grains to regions of lower extinction and density, where their mantles are released back into the gas, either by evaporation or photodesorption. As an example, gas-phase CO in the cloud center is over an order of magnitude more abundant in the $K = 10^{23} \text{ cm}^2 \text{ s}^{-1}$ models than in the models with no diffusion, while the grain mantle abundance of CO shows a corresponding drop (see Figure 5). Atomic oxygen, which rapidly destroys H₃⁺,

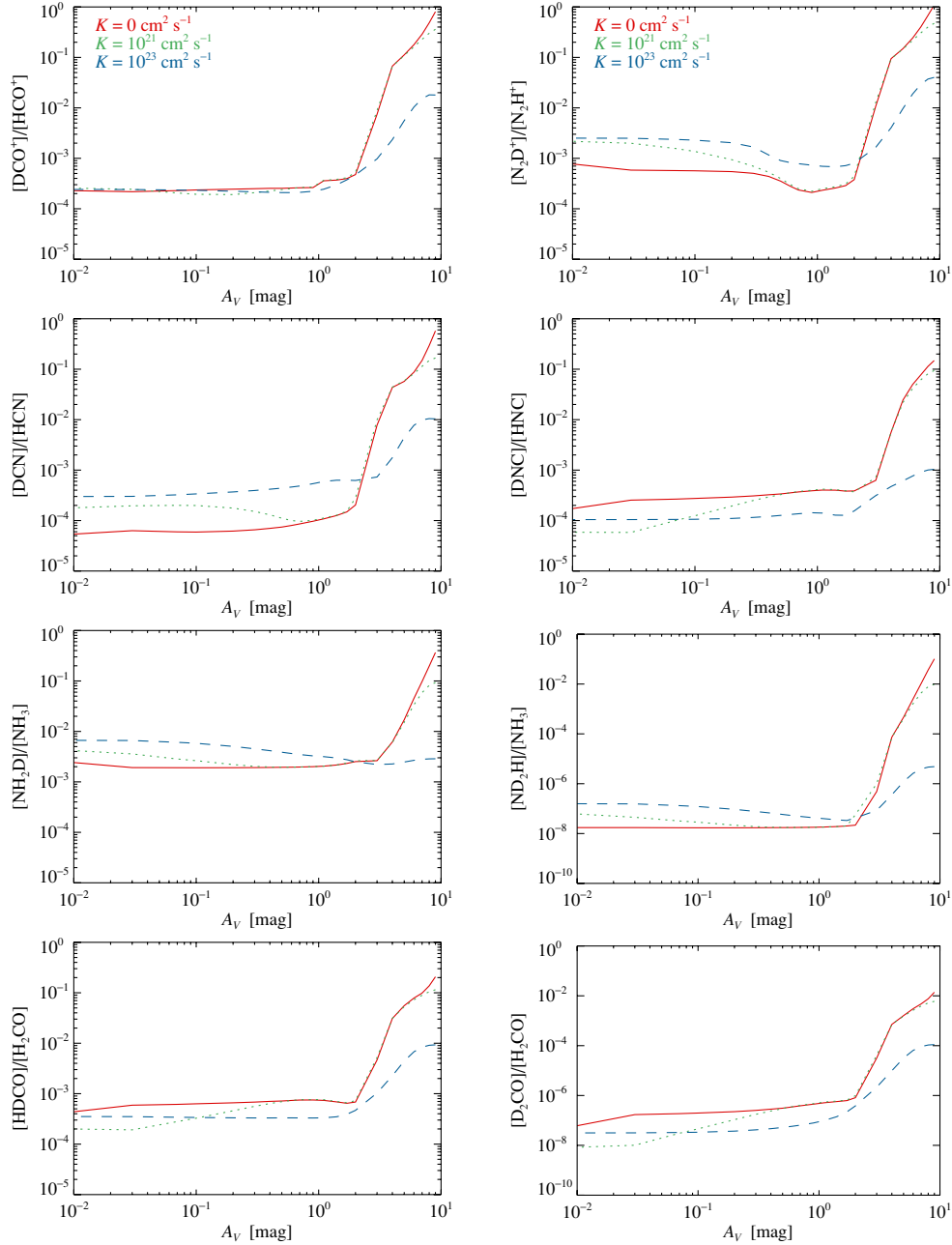


Figure 3. Fractionation ratios for DCO^+ , N_2D^+ , DCN , DNC , NH_2D , ND_2H , HDCO , and D_2CO (from top left to bottom right, respectively) for diffusion coefficients of $K = 0$, 10^{21} , and $10^{23} \text{ cm}^2 \text{ s}^{-1}$ (red solid, green dotted, and blue dashed lines, respectively). All plots show results for model 1 at $t = 1 \text{ Myr}$.

(A color version of this figure is available in the online journal.)

is 700 times more abundant in the $K = 10^{23}$ model because its freeze-out onto grains is reduced.

The combination of increased electron abundance and decreased freeze-out in the presence of turbulent diffusion leads to significantly lower abundances of H_3^+ and its deuterated analogs, compared to models with no diffusion. This in turn leads to lower abundances of the deuterated molecules that are formed from these ions. These trends are illustrated in Figure 6, which shows the abundances of H_3^+ , H_2D^+ , and D_2H^+ dropping as the level of turbulent diffusion rises. Comparing models with $K = 0$ and $K = 10^{23} \text{ cm}^2 \text{ s}^{-1}$, the abundances of H_3^+ , H_2D^+ , and D_2H^+ at the cloud center drop by factors of approximately 10, 30, and 200, respectively, when turbulent diffusion is active (for model 1 parameters; the results for model 2 show a similar trend).

Dissociative recombination of H_2D^+ and its multiply deuterated isotopologues is also the primary source of D atoms in the cloud center. As their abundances are lowered under the presence of turbulent diffusion, so too is the abundance of atomic deuterium—by a factor of $\sim 10^4$ when $K = 10^{23} \text{ cm}^2 \text{ s}^{-1}$. The lower abundance of D then inhibits the deuteration of molecules on grain surfaces, which proceeds via deuteron addition to mantle species. Since the high levels of deuteration observed toward low-luminosity protostars are often attributed to evaporation of mantle species following active grain surface chemistry (e.g., Loinard et al. 2001; Roberts et al. 2003), the role of turbulent diffusion in limiting grain surface deuteration may have implications for the degree of fractionation seen in the gas phase at later stages of protostellar evolution.

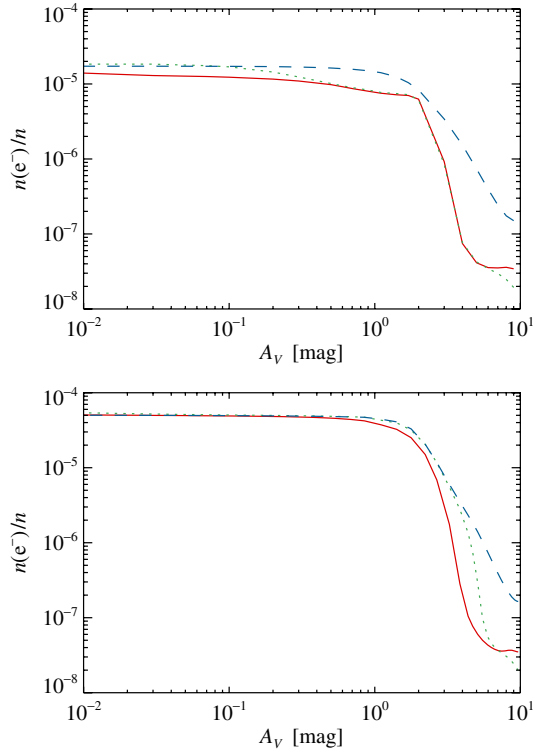


Figure 4. Electron fractional abundances for diffusion coefficients of $K = 0$, 10^{21} , and $10^{23} \text{ cm}^2 \text{ s}^{-1}$ (red solid, green dotted, and blue dashed lines, respectively). The results for model 1 are shown in the top plot and those for model 2 in the bottom, both at $t = 1 \text{ Myr}$.

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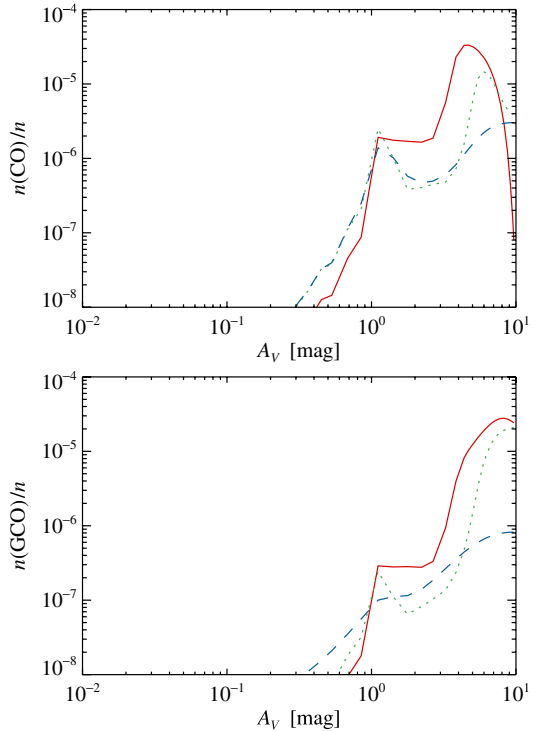


Figure 5. Fractional abundance of CO, both in the gas phase and on grain surfaces (referred to as GCO), for diffusion coefficients of $K = 0$, 10^{21} , and $10^{23} \text{ cm}^2 \text{ s}^{-1}$ (red solid, green dotted, and blue dashed lines, respectively). The results shown are for model 2 at $t = 1 \text{ Myr}$.

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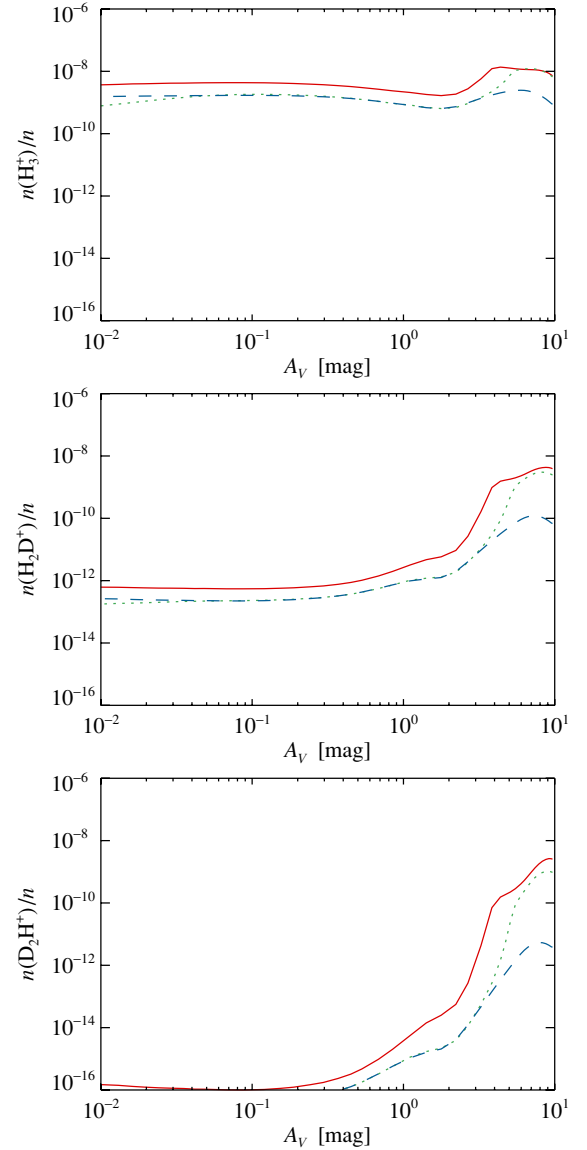


Figure 6. Fractional abundances of H_3^+ , H_2D^+ , and D_2H^+ for diffusion coefficients of $K = 0$, 10^{21} , and $10^{23} \text{ cm}^2 \text{ s}^{-1}$ (red solid, green dotted, and blue dashed lines, respectively). The results shown are for model 2 at $t = 1 \text{ Myr}$.

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3.3. Cloud Envelope

At the cloud edge, diffusion affects the typical cloud chemistry by supplying fresh molecular gas to be photodissociated/photoionized by the incident FUV photons, the products of which are then carried into the cloud interior. This increases the depth at which the gas becomes molecular, shifting the locations of the H/H_2 and $\text{C}^+/\text{C}/\text{CO}$ transitions that are characteristic features in models of cloud edges. However, the influence of turbulent diffusion is not uniform on all species. An interesting result of this is that the location of the H/H_2 transition can occur deeper into the cloud than that of D/HD , despite the latter's weaker shielding against photodissociation. The reason for this lies in the importance of the abundance gradient in determining the rate of diffusion. Since the elemental abundance of hydrogen is orders of magnitude above that of deuterium, the abundance gradients of H and H_2 at the cloud edge, where the abundance of H_2 drops rapidly from 0.5 to $\sim 10^{-3}$, are much

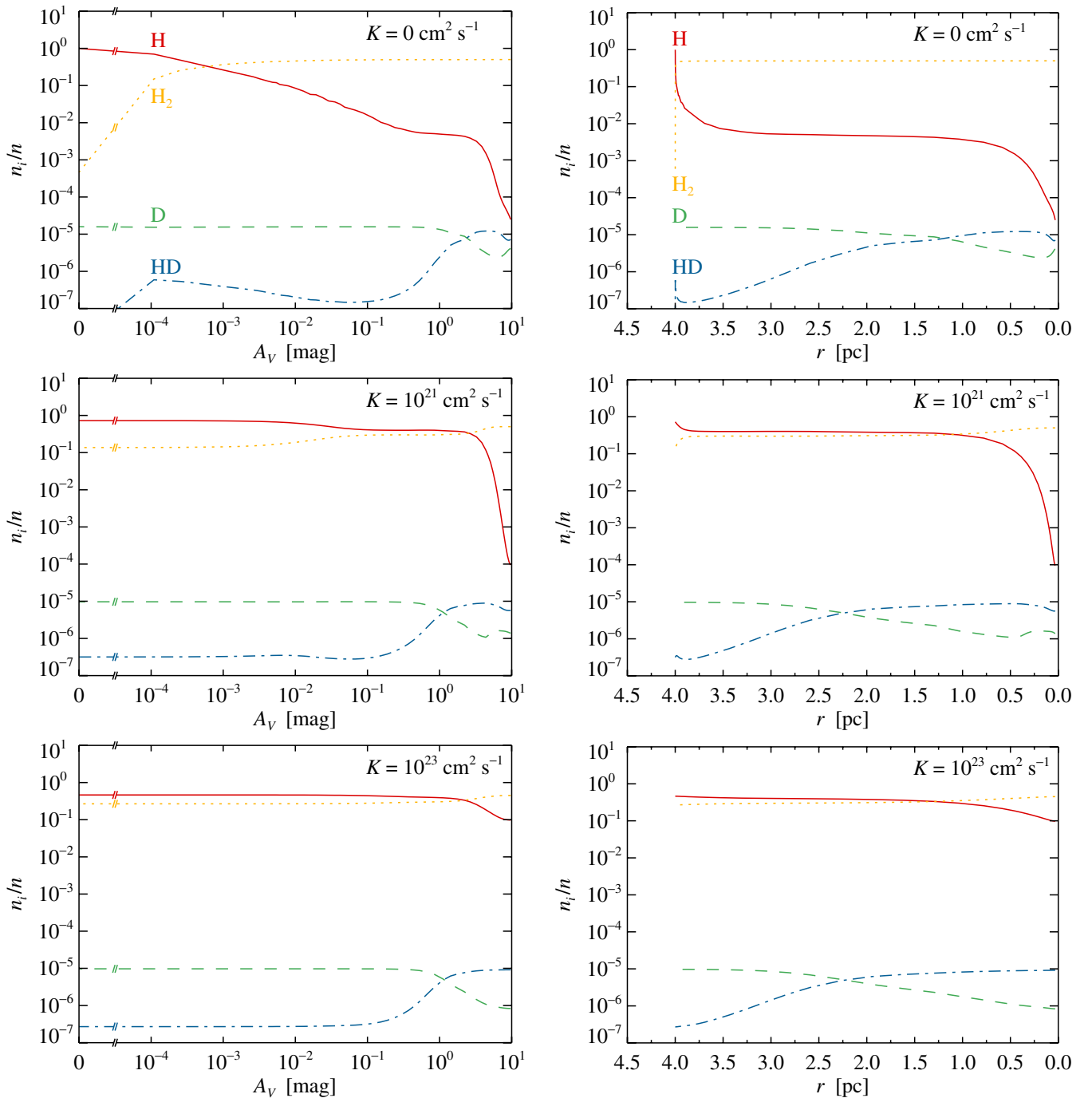


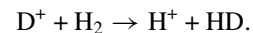
Figure 7. Fractional abundances of H, H_2 , D, and HD (red solid, yellow dotted, green dashed, and blue dot-dashed lines, respectively) for diffusion coefficients of $K = 0$, 10^{21} , and $10^{23} \text{ cm}^2 \text{ s}^{-1}$, from top to bottom. The results shown are for model 2 at $t = 1 \text{ Myr}$.

(A color version of this figure is available in the online journal.)

steeper than those of D and HD. This is illustrated in Figure 7, where the abundances of H, H_2 , D, and HD are shown as a function of visual extinction into the cloud for models with diffusion coefficients of $K = 0$ to $10^{23} \text{ cm}^2 \text{ s}^{-1}$. The inward flux of atomic hydrogen from the cloud surface, where it is produced by photodissociation of (primarily) H_2 , is over four orders of magnitude greater than the inward flux of atomic deuterium. This has the effect of “smearing out” the otherwise sharp H/ H_2 transition to such an extent that the depth at which H and H_2 have equal abundances increases from $A_V \sim 7 \times 10^{-4}$ ($K = 0$) to $A_V \sim 2$ ($K = 10^{23}$). In contrast, the equivalent position for

D and HD moves only slightly, and in the opposite direction, from $A_V \sim 2$ to $A_V \sim 1 \text{ mag}$.

Under typical interstellar conditions, molecular hydrogen is believed to form exclusively on grain surfaces. HD, however, is not only formed on grains, but can also form efficiently in the gas phase by the reaction



Indeed, in the warm diffuse cloud envelope, where the D^+ abundance is high due to charge exchange between D and H^+ , and H_2 begins to become abundant, this gas-phase reaction

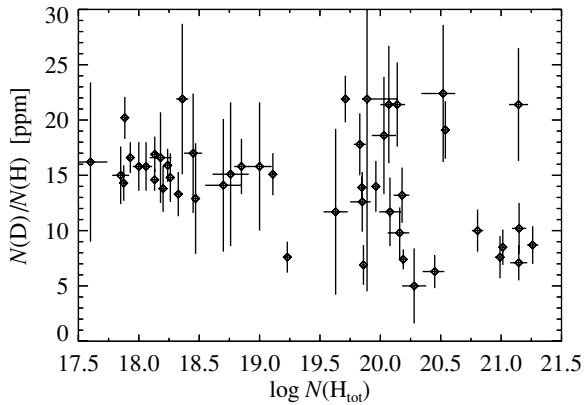


Figure 8. Observed galactic [D]/[H] ratios as a function of line-of-sight total hydrogen column density [$N(\text{H}_{\text{tot}}) = N(\text{H I}) + 2N(\text{H}_2)$]. See Table 4 for more details and references.

becomes the dominant formation route for HD. The jump in the HD abundance near the cloud edge ($A_V \sim 10^{-4}$ mag, $r \sim 4$ pc), seen in the top two plots of Figure 7, is due to the combination of high abundances of both D^+ (not shown) and H_2 at this point; nearer to the cloud surface, H_2 is less abundant due to photodissociation, and further into the cloud, D^+ drops in abundance, due to the declining abundance of H and thus H^+ , from which D^+ forms.

With the introduction of turbulent diffusion, the abundance gradient of D^+ is smoothed out, such that its abundance remains more constant across the cloud envelope and is a factor of ~ 3 higher at $A_V = 1$ mag when $K = 10^{23}$. This, in turn, leads to increased gas-phase formation of HD at this cloud depth, resulting in a higher HD abundance and thus explaining the outward shift in the location of the D/HD transition. This change is relatively insensitive to the strength of turbulent diffusion; models with $K = 10^{21}$ and $K = 10^{23} \text{ cm}^2 \text{ s}^{-1}$ produce nearly identical changes in the D^+ and HD abundances at this cloud depth.

While the diffusive process acts to redistribute atomic species throughout the cloud, it also brings molecular material from the interior out to the envelope of the cloud. This allows certain deuterated species to attain higher abundances within the region of low extinction than can be produced by static cloud models, where the effects of photodissociation, lower density, and higher temperature inhibit the formation of such species. A notable example of this is N_2D^+ , which shows an abundance enhancement of almost an order of magnitude when $K = 10^{23} \text{ cm}^2 \text{ s}^{-1}$, compared to the static cloud model (at $A_V \sim 10^{-2}$ mag).

We note that observations of H_3^+ in diffuse clouds (e.g., McCall et al. 2003; Indriolo et al. 2007) suggest that large low-energy cosmic-ray ionization rates are needed to explain the observed high abundances. These rates are up to an order of magnitude greater than the standard rate considered in our model. Although it is beyond the scope of this paper to examine the possible influence of varying model parameters such as the cosmic-ray ionization rate on the deuterium chemistry, it is worth mentioning that an order of magnitude increase in the rate would lead to higher H_3^+ and electron abundances in the model, which would likely reduce the level of deuteration that could be achieved. Since turbulent diffusion is effective at redistributing species between the cloud core and envelope, this would likely lead to an overall reduction in the level of deuteration throughout the cloud.

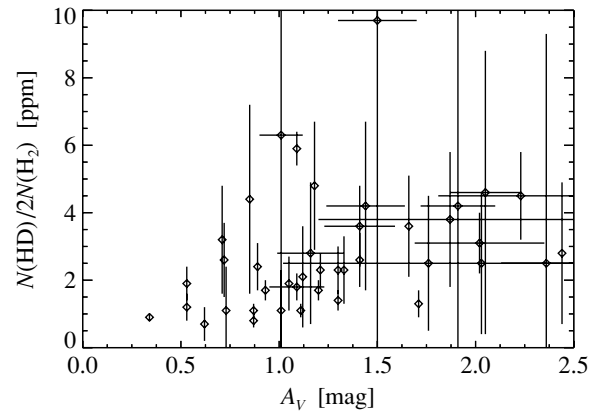


Figure 9. Observed galactic [HD]/2[H₂] ratios as a function of line-of-sight visual extinction [$A_V = R_V \cdot E(B - V)$]. See Table 5 for more details and references.

4. IMPLICATIONS FOR THE OBSERVED D/H RATIO

The galactic atomic D/H ratio has been studied extensively by observing absorption lines of D I and H I toward background stars in the local ISM. In the past, the lines of sight were restricted to nearby stars ($d \lesssim 200$ pc) by the sensitivity limits of the *Copernicus* and *Hubble Space Telescope* instruments, but with the launch of the *Far-Ultraviolet Spectroscopic Explorer* (*FUSE*) satellite, absorption studies along sightlines to stars several kpc away became possible. Figure 8 and Table 4 show a compilation of the observed galactic D/H ratios, taken primarily from the compilation of Linsky et al. (2006), but with more recent measurements added. The scatter in observed values is significant, with some measurements up to a factor of two above or below the mean value.

More recently, the molecular D/H ratio, defined as $[\text{HD}]/2[\text{H}_2]$, has begun to be examined in more detail, since *FUSE* allows sightlines containing significant fractions of molecular material to be probed. Figure 9 and Table 5 show a compilation of the observed galactic $[\text{HD}]/2[\text{H}_2]$ ratios, taken primarily from Snow et al. (2008), but updated with more recent data.

Let us now assume that our model cloud intersects a line of sight toward a background star and that we measure the column densities of H I and D I seen in absorption through the cloud. Given the abundance profiles of H, H_2 , D, and HD discussed in the previous section, what atomic D/H ratios might we expect at different points within the cloud? If the cloud consisted purely of atomic gas, measurements along any line of sight through it would yield the true elemental D/H ratio (i.e., that specified as an input to the model). However, if we consider a model cloud containing cold, dense material, much of the hydrogen and deuterium will be contained in molecules, either in the gas phase or on grain mantles. In this case, the measured atomic D/H ratio will no longer necessarily reflect the true elemental D/H ratio. Instead, it will reflect the remaining amount of hydrogen and deuterium in atomic form along a particular sightline, and will no longer “see” the deuterium and hydrogen contained in molecules. At this point, the measured D/H ratio becomes dependent upon the various chemical reactions that form and remove atomic deuterium and hydrogen. Due to the mass difference between these isotopologues, the formation and destruction rates for H- and D-bearing species will differ at low temperatures as a result of fractionation, and the fraction of each that remains in atomic form will strongly depend

Table 4
Compilation of Observed Galactic [D]/[H] Ratios

Target	d (pc)	$\log N(\text{H I})$	[D]/[H] (ppm)
Sirius	3	17.60	16.2 ± 7.2
36 Oph	6	17.85	15.0 ± 2.5
ϵ Eri	3	17.88	14.3 ± 1.6
31 Com	94	17.88	20.2 ± 1.9
H ζ 43	68	17.93	16.6 ± 1.4
ϵ Ind	4	18.00	16.0 ± 2.0
Procyon	4	18.06	16.0 ± 2.0
β Cas	17	18.13	16.9 ± 1.6
HR 1099	29	18.13	14.6 ± 1.0
G191–B2B	69	18.18	16.6 ± 4.1
β CMa	153	18.20	≥ 16
σ Gem	37	18.20	13.8 ± 2.1
Capella	13	18.24	15.9 ± 1.5
β Gem	10	18.26	14.8 ± 2.2
α Tri	20	18.33	13.3 ± 2.0
β Cet	29	18.36	21.9 ± 6.8
λ And	26	18.45	17.0 ± 5.0
Feige 24	74	18.47	13.0 ± 5.0
WD 0621–376	78	18.70	14.1 ± 6.0
WD 2211–495	53	18.76	15.1 ± 6.5
WD 1634–573	37	18.85	15.8 ± 2.5
α Vir	80	19.00	15.8 ± 8.0
GD 246	79	19.11	15.1 ± 1.9
λ Sco	216	19.23	7.6 ± 1.8
β Cen	161	19.63	11.7 ± 7.5
γ Vel	258	19.71	21.8 ± 2.1
α Cru	98	19.85	12.6 ± 3.6
BD +28 4211	104	19.85	13.9 ± 1.0
Lan 23	122	19.89	21.9 ± 10.8
μ Col	400	19.86	6.9 ± 6.9
ζ Pup	429	19.96	14.0 ± 2.3
TD1 32709	520	20.03	18.6 ± 5.3
WD 1034 + 001	155	20.07	21.4 ± 5.3
BD +39 3226	290	20.08	11.7 ± 3.1
Feige 110	179	20.14	21.4 ± 5.7
γ Cas	188	20.16	9.8 ± 2.7
ι Ori	407	20.15	14.1 ± 2.8
δ Ori	281	20.19	7.4 ± 1.2
θ Car	135	20.28	5.0 ± 3.4
ϵ Ori	412	20.45	6.3 ± 1.8
PG 0038 + 199	297	20.48	19.1 ± 2.6
LSE 44	554	20.52	22.4 ± 9.0
JL 9	590	20.78	10.0 ± 1.9
HD 195965	794	20.95	8.5 ± 1.6
LSS 1274	580	20.98	7.6 ± 1.9
HD 191877	2200	21.05	7.8 ± 2.4
HD 41161	1253	21.08	21.6 ± 5.1
HD 53975	1318	21.14	10.2 ± 2.3
HD 90087	2740	21.22	8.7 ± 1.7

Notes. Data taken from Linsky et al. (2006), Oliveira & Hébrard (2006), and Ellison et al. (2007).

on the density and temperature of the cloud. Furthermore, if the cloud is immersed in an ISRF, the photodissociation of molecules by the impinging UV photons will also affect the amount of atomic deuterium and hydrogen present in the cloud envelope. The self-shielding of H_2 means that, as extinction into the cloud increases, its photodissociation rate falls off more rapidly than that of HD (for a detailed discussion, see Le Petit et al. 2002). This difference in shielding results in a significant fraction of atomic deuterium being maintained to greater cloud depth, whereas atomic hydrogen

Table 5
Compilation of Observed Galactic [HD]/2[H_2] Ratios

Target	d (pc)	A_V (mag)	$\log N(\text{H}_{\text{tot}})$	$f(\text{H}_2)$	[HD]/2[H_2] (ppm)
HD 12323	3900	0.72	21.29	0.21	2.6 ± 1.1
HD 15558	2187	2.44	21.69	0.32	2.8 ± 2.1
HD 24534	398	2.05	21.34	0.76	4.6 ± 4.2
HD 27778	220	1.01	21.34	0.56	6.3 ± 16.0
HD 45314	799	2.03	21.28	0.42	2.5 ± 2.1
HD 53367	247	1.76	21.65	0.51	2.5 ± 2.0
HD 73882	925	2.36	21.58	0.67	2.5 ± 6.8
HD 74920	1497	1.09	21.25	0.21	5.9 ± 0.5
HD 90087	2716	0.93	21.18	0.08	1.7 ± 0.3
HD 91651	3500	1.01	21.16	0.02	1.1 ± 1.2
HD 91824	4000	0.87	21.19	0.09	1.1 ± 0.2
HD 93204	2630	1.30	21.43	0.04	1.4 ± 0.3
HD 93205	2600	1.20	21.35	0.05	1.7 ± 0.3
HD 93206	2512	1.21	21.35	0.03	2.3 ± 0.5
HD 93222	2900	1.71	21.55	0.03	1.3 ± 0.4
HD 94493	3327	0.62	21.17	0.18	0.7 ± 0.5
HD 101131	709	1.05	1.9 ± 0.8
HD 101190	2399	0.89	21.29	0.27	2.4 ± 0.7
HD 101413	2399	1.12	21.34	0.22	2.1 ± 1.5
HD 101436	2399	1.18	21.34	0.22	4.8 ± 1.9
HD 104705	3898	0.73	21.16	0.12	1.1 ± 1.3
HD 110432	301	2.02	21.20	0.55	3.1 ± 0.9
HD 116852	4760	0.53	21.01	0.12	1.2 ± 0.4
HD 147888	136	1.91	21.71	0.18	4.2 ± 14.1
HD 148422	8836	0.85	21.23	0.16	4.4 ± 2.8
HD 149404	1380	2.23	21.57	0.33	4.5 ± 1.3
HD 152233	1905	1.33	21.37	0.17	2.3 ± 1.0
HD 152248	1758	1.66	3.6 ± 1.5
HD 152723	1905	1.41	21.49	0.13	2.6 ± 0.8
HD 161807	383	0.34	0.9 ± 0.1
HD 177989	4909	0.71	21.06	0.23	3.2 ± 1.6
HD 185418	950	1.16	21.56	0.47	2.8 ± 2.1
HD 192639	1100	1.87	21.47	0.32	3.8 ± 2.0
HD 199579	794	1.09	21.25	0.38	1.8 ± 0.4
HD 201345	1907	0.53	20.91	0.03	1.9 ± 0.5
HD 206267	850	1.41	21.54	0.42	3.6 ± 1.2
HD 207198	832	1.50	21.55	0.38	9.7 ± 10.6
HD 207538	832	1.44	21.58	0.43	4.2 ± 2.5
HD 224151	1355	1.11	21.45	0.26	1.1 ± 0.2
HD 303308	2630	1.30	21.50	0.11	2.3 ± 0.7
HD 308813	2398	0.87	21.26	0.22	0.8 ± 0.2

Notes. Data taken from Snow et al. (2008), with additional extinction and $N(\text{H}_2)$ data taken from Rachford et al. (2002, 2009). For targets without R_V data, a typical value of 3.1 is adopted when calculating the visual extinction [$A_V = R_V \cdot E(B - V)$].

rapidly transitions to molecular form. Model clouds containing density and temperature gradients, or being exposed to an external radiation field, will therefore yield depth-dependent D/H ratios.

Figure 10 shows the atomic D/H ratio determined from the ratio of abundances, [D]/[H], as a function of visual extinction and radius in our static cloud model (i.e., with no diffusion). It is clear that the chemical processes discussed above can lead to a dramatic variation of the D/H ratio within such a cloud, with values spanning four orders of magnitude across its radius. With increasing depth (or visual extinction) into the cloud, the D/H ratio is seen to rise sharply, as hydrogen rapidly transitions to H_2 due to its effective shielding, while the density of atomic deuterium remains high, with a more gradual transition from D to HD, owing to its poor shielding.

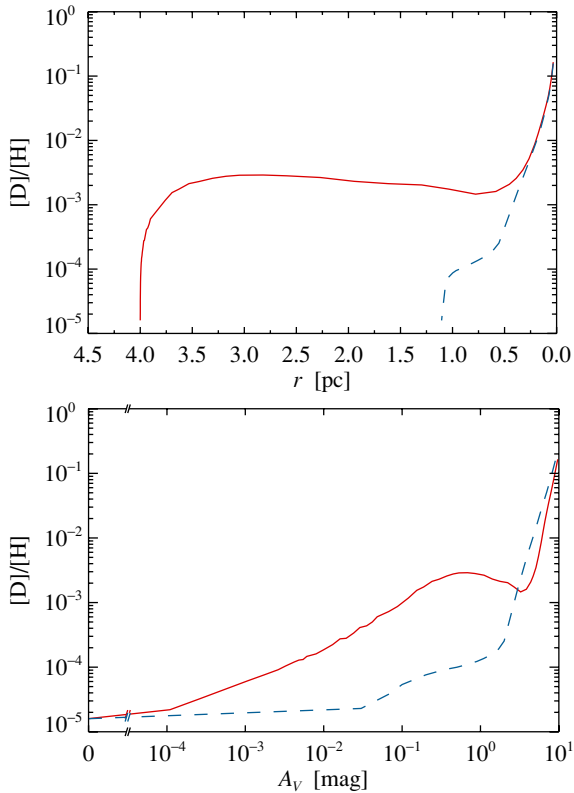


Figure 10. Atomic D/H ratio for static (i.e., no diffusion) versions of models 1 (blue, dashed) and 2 (red, solid), both at $t = 1$ Myr. The top plot shows the radial dependence of the D/H ratio and the bottom plot shows its variation as a function of visual extinction into the cloud.

(A color version of this figure is available in the online journal.)

Going deeper into the cloud, the atomic D/H ratio levels off as hydrogen becomes predominantly molecular and deuterium remains in atomic form, before the ratio begins to drop again, as deuterium, too, moves to molecular form (primarily HD). Finally, in the dark cloud interior ($A_V > 1$ mag), the D/H ratio starts to rise again as deuteration of H_3^+ and its subsequent dissociative recombination preferentially leads to the formation of D, rather than H, atoms in the cold dense core. Fractionation is so effective in the core that the atomic D/H ratio exceeds 0.1, a factor of 10^4 increase over the cosmic D/H ratio.

As we have seen in Section 3, introducing turbulent mixing to the model changes the amount of atomic deuterium and hydrogen present in the cloud by causing these atomic species to diffuse along their abundance gradients. Changes in the abundance of H and D due to turbulent diffusion lead to a corresponding change in the atomic D/H ratio. To examine the effect of increasing turbulent diffusion on the D/H ratio in the outer regions of the cloud, we focus our attention on the results of model 2, which includes a warm diffuse envelope that better represents the conditions at the edges of molecular clouds.

In Section 3.3, we showed that the abundances of atomic deuterium and hydrogen tend to drop at the cloud edge as the level of turbulence increases. This is due to their inward diffusion along the abundance gradients that are created by the H/H_2 and D/HD transitions. However, the strength of this diffusion is not the same for both species, and the abundance profile of atomic hydrogen is changed more significantly than that of atomic deuterium. This leads to changes in the atomic D/H ratio as the level of turbulent diffusion is increased, as shown in Figure 11.

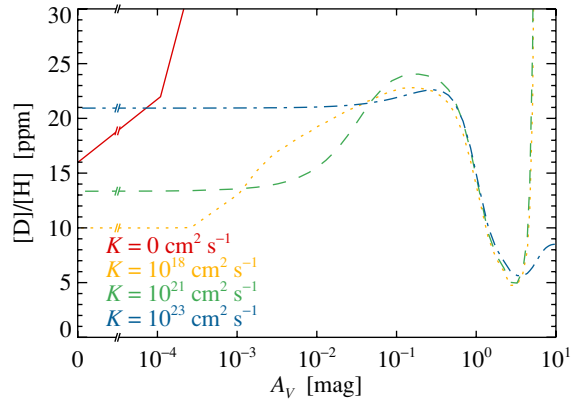


Figure 11. Atomic D/H ratio as a function of visual extinction into the cloud for diffusion coefficients of $K = 0, 10^{18}, 10^{21}$, and $10^{23} \text{ cm}^2 \text{ s}^{-1}$ (red solid, yellow dotted, green dashed, and blue dot-dashed lines, respectively). The results shown are for model 2 at $t = 1$ Myr.

(A color version of this figure is available in the online journal.)

At $K = 10^{18} \text{ cm}^2 \text{ s}^{-1}$, the D/H ratio at the cloud edge drops from the elemental value (16 ppm) to about 10 ppm. This is due to the drop in atomic deuterium abundance while the abundance of hydrogen remains relatively unchanged. As the level of turbulence increases, the inward diffusion of atomic hydrogen becomes more active and its abundance at the cloud edge begins to drop. Atomic deuterium is less affected, since its abundance gradient is smaller and occurs deeper into the cloud. The net result is that the D/H ratio begins to rise again, reaching 21 ppm when $K = 10^{23} \text{ cm}^2 \text{ s}^{-1}$, the maximum diffusion coefficient we consider here.

Deeper into the cloud, the introduction of turbulent diffusion smoothes out the abundance profiles of atomic deuterium and hydrogen, leading to less variation in the atomic D/H profile with cloud depth. In the cloud envelope ($A_V < 5$ mag), even a low level of turbulent mixing can dramatically reduce the variation of the D/H ratio, from over two orders of magnitude when no turbulent mixing is present to just a factor of ~ 4 when $K = 10^{18} \text{ cm}^2 \text{ s}^{-1}$. In the cloud core ($A_V \sim 10$ mag), turbulent diffusion has less effect on the atomic D/H ratio, which only drops by a factor of 10 when $K = 10^{21} \text{ cm}^2 \text{ s}^{-1}$, owing to the greater influx of atomic hydrogen and the reduced abundance of deuterated H_3^+ , the main source of D atoms in the cold dense core. Increasing the diffusion coefficient to $K = 10^{23} \text{ cm}^2 \text{ s}^{-1}$, however, causes the D/H ratio in the core to drop to ≈ 9 ppm, a factor of 10^4 reduction compared to the static model with no diffusion. Strong turbulence can therefore have a bigger impact on the atomic D/H ratio in the core. At this level of turbulence, diffusive mixing is so effective that the abundance of atomic hydrogen is fairly uniform across the cloud, varying by less than a factor of five, whereas, in the static model, it is nearly 10^5 lower at the core than at the edge.

The effect of varying the strength of turbulent diffusion in the model is therefore to produce a range of atomic D/H ratios at the cloud edge, with values spanning ~ 10 –20 ppm. In the cloud interior, increasing turbulence causes a more significant drop in the atomic D/H ratio, by up to four orders of magnitude in the case of strong diffusion ($K = 10^{23} \text{ cm}^2 \text{ s}^{-1}$).

If the lines of sight along which the galactic atomic D/H ratio has been measured are assumed to intersect diffuse gas at the edges of molecular clouds, the variation of the observed column densities of D I and H I (and therefore the inferred D/H ratio) will be dependent upon the degree of

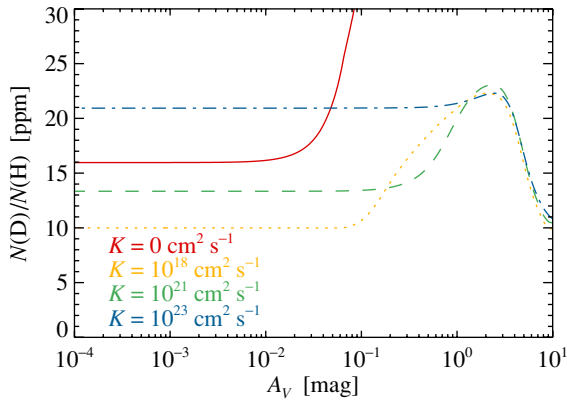


Figure 12. Integrated line-of-sight atomic D/H ratio through the model cloud, i.e., $N(D)/N(H)$, along sightlines of increasing extinction through the cloud, for diffusion coefficients of $K = 0, 10^{18}, 10^{21}$, and $10^{23} \text{ cm}^2 \text{ s}^{-1}$ (red solid, yellow dotted, green dashed, and blue dot-dashed lines, respectively). The results shown are for model 2 at $t = 1 \text{ Myr}$.

(A color version of this figure is available in the online journal.)

turbulent mixing within the clouds. Figure 12 shows the atomic D/H ratio that would be observed along a line of sight through a spherically symmetric model cloud, as a function of visual extinction through the cloud, for the case of no turbulent diffusion ($K = 0 \text{ cm}^2 \text{ s}^{-1}$) up to strong diffusion ($K = 10^{23} \text{ cm}^2 \text{ s}^{-1}$). It can be seen that, even for sightlines that intersect the cloud near its edge, the atomic D/H ratio can change by over a factor of two. If clouds exhibiting varying degrees of turbulent mixing are assumed to exist along different sightlines (as is almost certainly the case), this could help to account for the observed range of atomic D/H ratios.

Other mechanisms invoked to explain the observed variation in the atomic D/H ratio (in particular, depletion of deuterium onto dust grains or galactic infall of nearly pristine material) are expected to also produce variations in the observed metal abundances. In the case of the deuterium depletion model, the observed abundances of refractory metals are predicted to vary in line with that of deuterium, since they exhibit similar depletion onto grains. Conversely, increases in the D/H ratio produced by unmixed infalling low-metallicity material should be accompanied by decreased metal abundances. However, our turbulent diffusion models show only minor variations ($<5\%$) in the metal abundances (O I, Fe II, and Mg II) that would be observed at the cloud surface over the full range of turbulent diffusion coefficients considered. This suggests that there would be only a weak correlation between the D/H ratio and the metal abundances if turbulent diffusion were the sole cause of variation in the atomic D/H ratio.

Figure 13 shows the molecular D/H ratio determined from the ratio of abundances, $[HD]/2[H_2]$, as a function of visual extinction into the cloud. In comparison to the atomic D/H ratio, the molecular equivalent shows significantly less variation across the cloud (two orders of magnitude, instead of four orders of magnitude). In the static cloud model, the molecular D/H ratio attains the elemental D/H ratio (16 ppm) at the cloud edge, since the same unattenuated photodissociation rate is assumed for H_2 and HD, before dropping rapidly to $<1 \text{ ppm}$ when $A_V \gtrsim 10^{-4} \text{ mag}$, as self-shielding by H_2 causes its abundance to rise sharply. Deeper into the cloud ($A_V \sim 0.1 \text{ mag}$), the abundance of HD begins to rise, as the density increases and its rate of photodissociation starts to drop off, while the abundance of H_2 remains fairly constant. This leads to a steady increase in the $[HD]/2[H_2]$ ratio, which peaks at about 12 ppm. In the

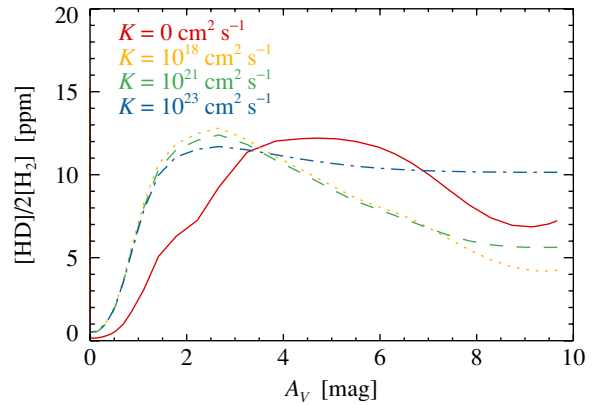


Figure 13. Molecular $[HD]/2[H_2]$ ratio as a function of visual extinction into the cloud for diffusion coefficients of $K = 0, 10^{18}, 10^{21}$, and $10^{23} \text{ cm}^2 \text{ s}^{-1}$ (red solid, yellow dotted, green dashed, and blue dot-dashed lines, respectively). The results shown are for model 2 at $t = 1 \text{ Myr}$.

(A color version of this figure is available in the online journal.)

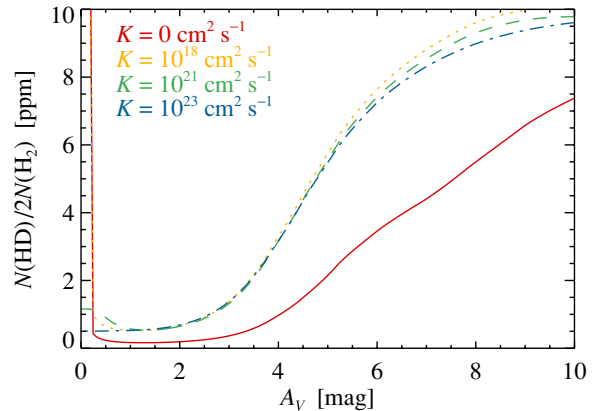


Figure 14. Integrated line-of-sight molecular D/H ratio through the model cloud, i.e., $N(HD)/2N(H_2)$, along sightlines of increasing extinction through the cloud, for diffusion coefficients of $K = 0, 10^{18}, 10^{21}$, and $10^{23} \text{ cm}^2 \text{ s}^{-1}$ (red solid, yellow dotted, green dashed, and blue dot-dashed lines, respectively). The results shown are for model 2 at $t = 1 \text{ Myr}$.

(A color version of this figure is available in the online journal.)

cloud core, efficient fractionation transfers the deuterium from HD to other molecules (and to atomic D), and the molecular D/H ratio begins to fall again, reaching 7 ppm at the center.

The influence of turbulent diffusion on the molecular D/H ratio serves to lower the ratio at the cloud edge (to $\sim 1 \text{ ppm}$ when $K = 10^{21} \text{ cm}^2 \text{ s}^{-1}$), since the mixing is more effective at bringing H_2 to the cloud surface than HD. The outward shift of the D/HD transition caused by turbulent diffusion (see Section 3.3) means that $[HD]/2[H_2]$ begins to rise at lower A_V , and the ratio peaks at 2–3 mag, compared to 4–5 mag in the static cloud model. This shift is insensitive to the strength of turbulent diffusion. Changes in the level of fractionation brought about by turbulent mixing affect the amount of deuterium transferred from HD to other molecules and lead to molecular D/H ratios varying between 5 and 10 ppm at the cloud center.

Molecular D/H ratios determined from line-of-sight column densities through the model cloud, $N(HD)/2N(H_2)$, are shown as a function of line-of-sight visual extinction in Figure 14 for turbulent diffusion coefficients of 0 to $10^{23} \text{ cm}^2 \text{ s}^{-1}$. Comparing this figure to the observed molecular D/H ratios in Figure 9, which have been measured for sightlines showing up to 2.5 mag of extinction, it is clear that our models underpredict the ratio

by a factor of 3–4. However, models including some degree of turbulent mixing give the best agreement, with generally higher molecular D/H ratios over the observed range of A_V . It has been noted previously (Le Petit et al. 2002; Lacour et al. 2005) that models fail to match the observed values unless the bulk of the absorbing gas is assumed to be in a single, dense component. Since our model cloud possesses a fairly large envelope of diffuse and warm material, which dominates the line-of-sight column densities at low A_V , this could account for the difference. If the $[\text{HD}]/2[\text{H}_2]$ abundance ratios in Figure 13 are instead compared to the observations, somewhat better agreement is found at low visual extinction (<1 mag). The agreement worsens at higher extinction, though this may be due in part to the larger uncertainties on the observed values at higher A_V .

5. SUMMARY

We find that turbulent diffusion affects the cloud chemistry in the following ways.

1. The ionization fraction is enhanced in the cloud center, due to an influx of ions and electrons produced by photoionization at the surface.
2. Freeze-out of abundant gas-phase species, such as CO, is reduced, as grain mantles are photodesorbed and/or evaporated when they are brought to the cloud surface.
3. Abundances of H_2D^+ , D_2H^+ , and D_3^+ are reduced in the cloud center due to the higher ionization fraction and CO abundance.
4. The H/H_2 transition occurs significantly deeper into the cloud due to rapid inward transport of atomic hydrogen along the sharp abundance gradient caused by self-shielding of molecular hydrogen.
5. The D/HD transition is affected less by turbulent mixing, as the abundance gradients of D and HD are more gradual than those of H and H_2 (due to the lower elemental deuterium abundance and less effective shielding of HD).

These effects lead to generally lower abundances of deuterated molecules and to a corresponding drop in fractionation ratios. We find that turbulent diffusion causes atomic hydrogen to remain abundant deep into molecular clouds, while inhibiting the pathways that normally allow significant deuteration in the cold dense cores of these clouds. This is reflected in the atomic D/H ratio, which drops dramatically from $\sim 10^{-1}$ in the cloud center when $K = 0 \text{ cm}^2 \text{ s}^{-1}$ (i.e., no diffusion) to $\sim 10^{-5}$ when $K = 10^{23} \text{ cm}^2 \text{ s}^{-1}$. Close to the cloud edge, the atomic D/H ratio varies by over a factor of two as the level of turbulent mixing increases, with values spanning ~ 10 – 20 ppm, in agreement with the range of observed values. The impact of turbulent mixing on the molecular D/H ratio, $[\text{HD}]/2[\text{H}_2]$, is less significant, but nevertheless shows some dependence on the degree of turbulent mixing.

Based on these results, we propose a new process to help explain the significant scatter in the observed galactic atomic D/H ratio. If part of the intervening gas resides in the envelope of a molecular cloud, we expect the column densities of H I and D I near the cloud edge to be dependent on the degree of turbulent mixing within the cloud, leading to variations in the D/H ratio that would be observed.

In reality, various mechanisms are likely to be working in combination to produce the observed range of D/H ratios. Many of the parameters that govern the relative contribution of each process, such as the initial abundances, dust composition, turbulent diffusion coefficient, and ionization fraction, are

hard to determine with any precision, making it difficult to disentangle the various processes involved, or to say definitively if one process is dominating. The turbulent diffusion mechanism proposed here could be tested by searching for a correlation between observed D/H ratios and a proxy for the degree of turbulence along each line of sight, such as the turbulent linewidths of the absorption lines, although the analysis would be complicated by additional uncertainties due to overlapping absorption components and bulk cloud motions.

With the exception of galactic infall of low-metallicity material, all mechanisms that have so far been proposed to explain the variation in atomic D/H ratio result in lower values. Therefore, the appropriate value to adopt would be the largest observed, i.e., ~ 23 ppm in the Milky Way (e.g., Linsky et al. 2006). The turbulent mixing of atomic and molecular gas at the edges of molecular clouds discussed here is an alternative mechanism that can explain the scatter in atomic D/H ratios observed beyond the Local Bubble. However, in this case the observed D/H ratio can be either decreased or increased compared to the “true” elemental ratio, depending on the magnitude of the turbulent diffusion coefficient.

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